

#21
9-16-02
Payton**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE****In re United States Patent Application of:****Applicant:** Peter Van Buskirk, et al.**Application No.:** 09/200,495**Date Filed:** November 25, 1998**Title:** OXIDATIVE TOP
ELECTRODE DEPOSITION
PROCESS, AND
MICROELECTRONIC
DEVICE STRUCTURE**Docket No.:** 2771-337 RCE (7482)**Examiner:** S. Hu**Art Group:** 2811**FACSIMILE TRANSMISSION CERTIFICATE****ATTN: SHOUXIANG HU****Fax No. (703) 746-3922**

I hereby certify that this document is being filed in the United States Patent and Trademark Office, via facsimile transmission to Commissioner for Patents, Box AF, Washington, D.C. 20231, on August 1, 2002, to United States Patent and Trademark Office facsimile transmission number (703) 746-3922.

16

Number of Pages of this Affidavit, including Exhibits

Steven J. Hultquist

August 1, 2002

Date

**AFFIDAVIT UNDER 37 C.F.R. §1.131 OF STEVEN J. HULTQUIST
IN U.S. PATENT APPLICATION NO. 09/200,495**

Commissioner for Patents
Box AF
Washington, DC 20231

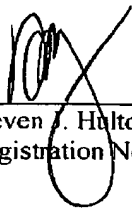
ATTN: Shouxiang Hu

Sir:

I, **STEVEN J. HULTQUIST**, being duly sworn, depose and say:

1. THAT I am a patent attorney registered to practice before the United States Patent and Trademark Office, and an attorney of record in the above-identified U.S. Patent Application No. 09/200,495 filed November 25, 1998 in the names of Peter C. Van Buskirk, et al. ("Application").
2. THAT I have read and am familiar with the prosecution record of the Application, including the Declaration under 37 C.F.R. § 1.131 filed on May 6, 2002 in the U.S. Patent and Trademark Office for the Application ("Declaration").
3. THAT attached hereto as Exhibit A hereof is a true and exact copy of the pages of the Invention Disclosure document ("Invention Disclosure") whose corresponding pages containing blacked-out dates were attached to the Declaration as Exhibit 1 thereof, and that the true and exact copy of the pages of the Invention Disclosure attached hereto as Exhibit A hereof does not have such dates blacked-out.
4. THAT the true and exact copy of the pages of the Invention Disclosure attached hereto as Exhibit A hereof contains the date of signatures of the co-inventors Peter Van Buskirk, Steve Bilodeau and Stephen Johnston as June 8, 1998, the date of signatures of co-inventors Dan Vestyck and Michael Russell as June 11, 1998, and the date of signature by witness Margaret Chappuis as June 29, 1998, and that at the top of the first page of the Invention Disclosure, the document contains the legend "ROI Number 98-55" denoting the Record of Invention (ROI) number, 98-55, assigned thereto in the records of applicants' assignee, Advanced Technology Materials, Inc. ("ATMI").
5. THAT attached hereto as Exhibit B hereof is a true and exact copy of a fax transmittal cover sheet addressed to me from Maggie Chappuis, a patent agent of ATMI and the witness who signed the Invention Disclosure, that such fax transmittal cover sheet is dated July 17, 1998 and identifies the Invention Disclosure by Record of Invention (ROI) number 98-55 and by ATMI's File No. 337, and that such fax transmission cover sheet transmitted to me a copy of the Invention Disclosure, and noted that such copy of the Invention Disclosure was furnished "For new patent application."
6. THAT attached hereto as Exhibit C hereof is a true and exact copy of an email message to me dated August 28, 1998 from Maggie Chappuis, which attached an electronic copy of the Invention Disclosure as finalized, and contained the message that such Invention Disclosure, referred to in the subject heading of the email as ROI 98-55, was attached, "for conversion into a patent application" with the email message further requesting "a tentative date for completion of a first draft [of the requested patent application]."
7. THAT attached hereto as Exhibit D hereof is a true and exact copy of an email message from me dated September 28, 1998 and addressed to Oliver Zitzmann, ATMI's Chief Legal Officer, titled "Draft of ATM-337 (PC89000)," wherein portions of the second and third paragraphs embodying attorney-client confidential communication have been blacked out, that such email message states that "enclosed is a draft of ATM-337" referring to the fact that an initial draft of the Application as prepared by me was attached to the email message, with such attached initial draft of the Application specified iconically as "337_Application.DC" on the email message, and referring to the preliminarily prepared drawings of the Application by the statement in the email message that "The drawings for Figures 1-4 will be sent to you by fax in a few minutes."

8. THAT attached hereto as Exhibit E hereof is a true and exact copy of an email message dated November 13, 1998 from Margaret Chappuis to me, attaching a draft of the Application as specified iconically as "337_Application.DOC," stating that such draft of the Application was "revised by Mike Russell," a co-inventor for the Application, and requesting that I "make any necessary changes to ensure that the Applications [two applications were attached to the email] are in appropriate form for filing" and "return the Applications to Danbury [Danbury, Connecticut, the location of ATMI] for filing in the U.S. PTO."
9. THAT attached hereto as Exhibit F hereof is a true and exact copy of an email message dated November 24, 1998 from Margaret Chappuis to me, noting that the Application, identified in the email message by the file number ATM-337, "will be Express Mail filed in the U.S. PTO November 25, 1998."
10. THAT, consistent with the November 24, 1998 email message referred to in paragraph 9 above, the Application was filed in the U.S. PTO by Express Mail on November 25, 1998.
11. THAT the attached documents evidence the Invention Disclosure as having been executed by the inventors on June 8, 1998 and June 11, 1998, prior to the effective date, July 29, 1998, of Inoue, et al. U.S. Patent No. 6,300,212, and establish diligence of applicants and their attorney and assignee, from the execution by the inventors of the Invention Disclosure on June 8, 1998 and June 11, 1998, until filing of the Application in the U.S. Patent and Trademark Office on November 25, 1998.

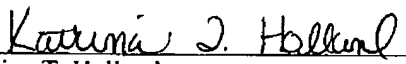

Steven J. Hultquist
Registration No. 28,021

COUNTY OF DURHAM

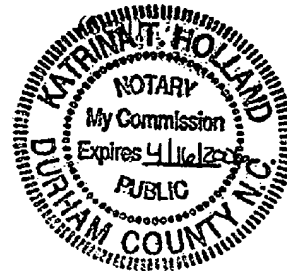
STATE OF NORTH CAROLINA

Sworn to and subscribed before me

this 1st day of August, 2002.


Katrina T. Holland

My Commission Expires: 4/16/2006



**INTELLECTUAL PROPERTY/
TECHNOLOGY LAW**

P.O. Box 14329
Research Triangle Park, NC 27709
Telephone: (919) 419-9350
Fax: (919) 419-9354
Attorney File: 2771-337 RCE (7482)

EXHIBIT A

AUG. 28. 1998 3:01PM

ATMI LEGAL DEPT

NO. 349

P. 2/4

Advanced Technology Materials, Inc., COMPANY CONFIDENTIAL INFORMATION

Page 1 of 2

INVENTION DISCLOSUREROI Number 98-55Oxidizing top electrode deposition process(1) State the PROBLEM or DEFICIENCY, which is overcome by your invention:

Ferroelectric and high ϵ thin films capacitors are becoming increasingly important in microelectronics, for use in advanced memories, as decoupling capacitors and infrared detectors, for example. The ferroelectric or high ϵ film is typically an oxide perovskite (or layered structure perovskite) such as PbZrTiO_3 , $(\text{Ba}, \text{Sr})\text{TiO}_3$ (or $\text{SrBi}_2\text{Ta}_2\text{O}_9$), although other similar materials are also used.

Properties of ferroelectric and high ϵ capacitors depend, in general, on the stoichiometry (atomic relative concentrations) of the film. Whilst the most common concern is the cation stoichiometry, film electrical properties are extremely sensitive to oxygen concentration as well.

Formation of the capacitor typically involves vacuum deposition of a metal on top of the oxide layer. It is likely that the top electrode (TE) deposition conditions will result in oxygen loss in the ferroelectric or high ϵ film, particularly at its surface. This oxygen loss may be due chemical or physical aspects of the TE deposition process. Chemical aspects include a higher affinity of O by the TE material (compared to the ferroelectric), or by another chemical driving force, such as the environment in a metal CVD process that may be used to deposit the TE. Physical effects include thermal desorption that could be stimulated by the transfer of energy of an incident atom, or by sputtering, whereby an adatom with superthermal energy (>1 eV) directly results in ejection of an O atom.

For dc magnetron sputtering of Ir (for example), adatom energies at the film surface can be on the order of 120 eV for Ar⁺, and 25 eV for Ir⁺. Since 200 eV Ar is known to modify the surface of crystalline Si to a depth of 28\AA , it is plausible that Ar bombardment in a magnetron deposition process will have significant effects on the surface of a ferroelectric such as PbZrTiO_3 .

While oxygen loss may in principle be compensated by post annealing in oxidizing conditions, this approach depends on the ability of the TE to allow O to diffuse from the annealing atmosphere to the ferroelectric film surface. Pt will allow O diffusion for that purpose, but other more desirable TE materials such as Ir and IrO_2 will not; they are good O diffusion barriers.

So a method is needed to prevent the ferroelectric or high ϵ film from becoming oxygen deficient during TE deposition.

(2) Describe clearly the INVENTION, RESULTS, ADVANTAGES. (Make DRAWINGS when possible and DESCRIBE FULLY the invention and its OPERATION using REFERENCE NUMERALS to indicate elements.INVENTOR(S):

(Signature)
Peter Van Bualdik
(Print Name)
June 8, 1998
(Date)

(Signature)
Steve Bilodeau
(Print Name)
June 8, 1998
(Date)

(Signature)
Stephen Johnston
(Print Name)
June 8, 1998
(Date)

(Signature)
Dan Vestreck
(Print Name)
June 11, 1998
(Date)

(Signature)
Michael Russell
(Print Name)
June 11, 1998
(Date)

READ AND UNDERSTOOD BY:

(Signature - Full Name)
Margaret Chappuis
(Print or Type Full Name)
June 28, 1998
(Date)

(Signature - Full Name)

(Print or Type Full Name)

(Date)

AUG.28.1998 3:03PM

ATMI LEGAL DEPT

NO.349

P.3/4

Advanced Technology Materials, Inc., COMPANY CONFIDENTIAL INFORMATION

Page 2 of 2

There are several ways to prevent oxygen deficiency in the ferroelectric film:


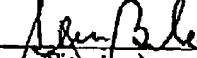

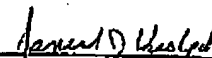

I. During TE deposition:

1. Sputter deposition of a metallic (non-oxide) TE in the presence of O. This method can use O₂, N₂O, NO₂, etc. for sputtering. Reactive sputtering with oxygen present is a well known way to deposit an oxide compound, but sputtering conditions such as pressure, substrate temperature and deposition rate can be often be adjusted to deposit a suboxide or pure metal even if oxygen is present. In those cases oxygen present in the working gas will tend to prevent a net loss of oxygen in the surface of the ferroelectric. Once the ferroelectric surface is covered, a different TE process can continue, with the oxygen source turned off for example. A pure metal TE may be desirable because it has a higher work function, which is known to reduce leakage in ferroelectric capacitors. Sputtered pure metal top electrodes often also have lower compressive stress than those sputtered in the presence of oxygen that may be desirable.
2. Evaporation of a noble metal in the presence of O, resulting in a metal TE, and a decreased tendency for the ferroelectric film to lose O during deposition. The rationale is the same as 1.
3. Minimize bombarding energy and flux during deposition by manipulating sputtering conditions, in order to minimize O loss from the surface, and to reduce physical damage to the lattice.
4. Process the ferroelectric surface so that it contains excess O, either in the lattice or in grain boundaries. This may be achieved by ion implantation of O at energies greater than 200 eV, either prior or subsequent to TE deposition.
5. Deposition of the noble metal TE (typically Ir or Pt or alloys containing those species) using a CVD process that incorporates oxygen, such as that described in the USP Applications by T. Baum et al., ATM-207/207D: "Platinum source compositions for CVD of Pt"
6. Deposition of a noble metal and an oxide compound mixed film, especially one that may "give up" its O easily, such as MnO, CeO₂, etc. In that way O may be provided to the ferroelectric surface without a long diffusion path through the metallic electrode.

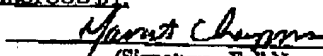
II. During the PZT process

7. Terminate the PZT deposition process under oxygen-excess conditions.
8. Terminate the PZT deposition process under low oxygen conditions resulting in a "metallic capping" layer that may reduce oxygen mobility/depletion in the ferroelectric film. The "capping" layer can be etched in a pre-TE step under conditions that minimize surface depletion of oxygen thereby exposing the desired PZT film.

INVENTOR(S):

				
(Signature)	(Signature)	(Signature)	(Signature)	(Signature)
Peter Van Buelck	Steve Blodau	Stephen Johnston	Dan Vastek	Michael Russell
(Print Name)	(Print Name)	(Print Name)	(Print Name)	(Print Name)
June 8, 1998	June 8, 1998	June 8, 1998	June 11, 1998	June 11, 1998
(Date)	(Date)	(Date)	(Date)	(Date)

READ AND UNDERSTOOD BY:


 (Signature - Full Name)
 Margaret Chappuis
 (Print or Type Full Name)
 June 29, 1998
 (Date)

 (Signature - Full Name)

 (Print or Type Full Name)

 (Date)

EXHIBIT B

AUG. 28. 1998 3:01PM

ATMI LEGAL DEPT

NO. 349

P. 1/4

FAX TRANSMISSION

**Advanced Technology Materials**7 Commerce Drive ♦ Danbury, CT 06810-4169
Phone 203-794-1100 ♦ Fax 203-792-8040

TO: Steven Hultquist

COMPANY: IPTL

FROM: Maggie Chappuis

DATE AND TIME OF TRANSMISSION: 7/17/98

MESSAGE:


ROI Number 98-55, "Oxidizing Top Electrode Deposition Process"
ATMI File: 337
For new patent application

THE DOCUMENT(S) ACCOMPANYING THIS FACSIMILE TRANSMISSION CONTAINS INFORMATION WHICH IS CONFIDENTIAL AND/OR LEGALLY PRIVILEGED. THE INFORMATION IS INTENDED ONLY FOR THE USE OF THE INDIVIDUAL OR ENTITY NAMED ON THIS TRANSMISSION SHEET. IF YOU ARE NOT THE INTENDED RECIPIENT, YOU ARE HEREBY NOTIFIED THAT ANY DISCLOSURE, COPYING, DISTRIBUTION OR THE TAKING OF ANY ACTION IN RELIANCE ON THE CONTENTS OF THIS FAXED INFORMATION IS STRICTLY PROHIBITED, AND THE DOCUMENT(S) SHOULD BE RETURNED TO THIS COMPANY. IF YOU HAVE RECEIVED THIS FACSIMILE IN ERROR, PLEASE NOTIFY US BY TELEPHONE IMMEDIATELY SO THAT WE CAN ARRANGE FOR THE RETURN OF THE ORIGINAL DOCUMENTS AT NO COST TO YOU.

FAX NO: 919/419-9354

This transmission is 4 pages including cover page.

EXHIBIT C

 Maggie Chappuis
08/28/98 02:41 PM

To: Steve Hultquist/ATMI@ATMI
cc: Oliver Zitzmann/ATMI@ATMI, Michael Russell/ATMI@ATMI
Subject: ATMI ROI 98-55 "Oxidizing Top Electrode Deposition Process"
ATMI File: 337

Steven,

Attached is the ROI referenced above for conversion into a patent application. The project code is 89000. Mike Russell is gathering the references and I will mail or fax them as soon as they are in hand.

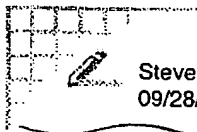

Oxidizing top electrode deposition proces

At your convenience please provide us with a tentative date for completion of a first draft.

A faxed copy of the ROI will follow.

Mag Chappuis

EXHIBIT D



Steve Hultquist
09/28/98 03:50 PM

To: Oliver Zitzmann/ATMI
cc:
Subject: Draft of ATM-337 (PC89000)

As promised earlier today, enclosed is a draft of ATM-337.

I think that the application would [REDACTED]
[REDACTED]
[REDACTED]
[REDACTED]

[REDACTED]
337_Application.DC

We have taken the position that [REDACTED]
[REDACTED]

The drawings for Figures 1-4 will be sent to you by fax in a few minutes.

Steven

EXHIBIT E

27 11-331

Steven J. Hultquist

From: mchappui@atmi.com
Sent: Friday, November 13, 1998 5:16 PM
To: hultquist@iptl.com
Subject: ATM-322 and ATM-337



322+315.doc



ATT00002.txt



337_Application.DOC

Steven,

Attached are two patent application drafts for your review. Both were revised by Mike Russell. Please make any necessary changes to ensure that the applications are in the appropriate form for filing.
(See attached file: 322+315.doc)(See attached file: 337_Application.DOC)

In the first application 322+315, Mike has combined the subject matter of ATM-315, "Stop Layers for CMP of FeRAM Capacitor Structures" and ATM-322, "Novel Polishing Media for CMP of Ferroelectric Capacitors". I have assigned this new application, file number ATM-322.

After your review, please return the applications to Danbury for filing in the U.S. PTO.

Please let me know if you have any questions.

Have a nice weekend.

Mag Chappuis

(UUEncoded file named: 322+315.doc follows)
(Its format is: Lotus Manuscript 1.0)

EXHIBIT F

Steven J. Hultquist

To: mchappui@atmi.com; Oliver Zitzmann Esquire (E-mail)

Subject: RE: ATM-322 and ATM-337

Thanks. I will calendar November 25, 1999 as the foreign filing deadline.

Steven

-----Original Message-----

From: mchappui@atmi.com [mailto:mchappui@atmi.com]

Sent: Tuesday, November 24, 1998 5:35 PM

To: hultquist@iptl.com

Cc: ozitzmann@atmi.com; mrussell@atmi.com

Subject: ATM-322 and ATM-337

The patent applications corresponding to the ATMI files referenced above will be Express Mail Filed in the U.S. PTO November 25, 1998.

Copies were First Class mailed to you.

Mag Chappuis